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(54) **Pneumatic tires.**

(57) A pneumatic tire has a tread composed of a rubber composition which includes a rubber component and particulates of a crystalline syndiotactic-1,2-polybutadiene resin. The particulates have an average particle diameter of 10 to 500 μm, and the melting point of said crystalline syndiotactic-1,2-polybutadiene resin is not less than 110°C. The compounding ratio of the resin is 5 to 60 parts by weight relative to 100 parts by weight of the rubber composition. A matrix portion of the tread rubber other than the above particulates is preferably a foamed rubber. The particulates may be resin-composite particulates composed of the crystalline syndiotactic-1,2-polybutadiene resin having a melting point of not less than 110°C and a carbon black, wherein the compounding ratio of the resin-composite particulates is 5 to 60 parts by weight relative to 100 parts by weight of the rubber component, and the resin and the carbon black satisfy the following inequalities: $250 < X + 10\,Y < 1300$ in which X is nitrogen-adsorption specific surface area (unit: m^2g) and Y is compounding ratio of the carbon black (parts by weight) relative to 100 parts by weight of the resin.

EP 0 517 538 A1

The present invention relates to pneumatic tires, more particularly, so-called all season type pn umatic tires which have remarkably improved drivability, brakability and cornering stability on ice and snow roads without deteriorating cornering stability or durability in th summer season.

Recently, demands have been increasing for so-called all season type tires which can be used even in the winter season, without b ing xchanged, as in the summ r season. Such tires are required to possess substantially the same dry gripping power, wet gripping power, cornering stability, durability and low fuel consumption even in the winter season as well as in the summer season, and also to possess sufficient drivability and brakability even on ice and snow.

A tread rubber used in such tires needs to satisfy requirements for a tread rubber required in the summer season, and also its hardness at low temperatures needs be lowered. In view of this, methods have been formerly known to use a polymer having a low glass transition temperature or employ a softener or plasticizer capable of appropriately keeping modulus of elasticity at low temperatures.

However, although the former method exhibits some improvement on tire performances in a ice-snow temperature range due to a hysteresis loss characteristic of such a polymer, brakability or cornering stability is unfavorably insufficient on wet or dry roads. The latter method is disclosed in Japanese Patent application Laid-open No. 55-135,149, 58-199,203 or 60-137,945, and it is pointed out that any of the techniques of these publications has a problem that as compared with an improved degree of the performances on ice and snow, wear resistance or durability on running on general roads are more adversely affected.

Although relatively excellent tire performances on ice and snow are indeed exhibited on so-called dry-on-ice conditions, i.e., a relatively low temperature range not more than -5°C, in any of the above techniques, a sufficient coefficient of friction cannot be obtained with respect to tire performances on ice and snow in a wet state near 0°C, i.e., in a so-called wet-on-ice conditions. Therefore, it cannot be said that drivability, brakability and cornering stability are fully improved with respect to the wet-on-ice conditions.

It is an object of the present invention to provide a pneumatic tire called an all season type pneumatic tire in a strictly actual sense, which can not only fully maintain cornering stability, durability and low fuel consumption in the summer season but also have satisfactory drivability and brakability both in the dry-on-ice conditions and in the wet-on-ice conditions.

The present inventors have strenuously investigated performances of rubbers of treads of the above-mentioned all season or studless tires on ice and snow, particularly on ice and snow roads in a wet state, and have discovered that when a rubber composition including particulates of a syndiotactic-1,2-polybutadiene resin having a specific structure is used as a rubber composition of the tread, tire performances on ice and snow can be remarkably improved, while cornering stability, durability, etc. required in the summer season or in running on ordinary roads are not deteriorated. The present invention has been accomplished based on this discovery.

That is, the pneumatic tire according to the present invention is characterized in that a rubber composition is used for a tread, which rubber composition includes a rubber component and particulates of a crystalline syndiotactic-1,2-polybutadiene resin or particulates of specific syndiotactic-1,2-polybutadiene resin-composite material, the particulates having an average particle diameter of 10 to 500 μm and a melting point of said crystalline syndiotactic-1,2-polybutadiene resin being not less than 110°C, and a compounding ratio of the resin being 5 to 60 parts by weight relative to 100 parts by weight of the rubber component. The rubber component constituting a matrix portion of the tread rubber other than the above particulates is preferably a foamed rubber. In this case, it is confirmed that the tire performances on ice and snow can be further improved.

Further, the object of the present invention is attained by the pneumatic tire which uses, as a tread rubber, a rubber composition including a rubber component and resin-composite particulates having the average particle diameter of 10 to 500 μm and composed of a crystalline syndiotactic-1,2-polybutadiene resin having a melting point of not less than 110°C and a carbon black, a compounding ratio of the resin-composite particulates being 5 to 60 parts by weight relative to 100 parts by weight of the rubber component, and the resin and the carbon black satisfying the following inequations: $250 < X + 10Y < 1300$ in which X is a nitrogen-adsorption specific surface area (unit: m^2/g) and Y is the compounding ratio of the carbon black (parts by weight) relative to 100 parts by weight of the resin. According to this pneumatic tire, the rubber component constituting a matrix portion of the tread rubber composed of the above rubber composition other than the resin-composite particulates is preferably a foamed rubber.

The first aspect of the present invention will be now explained in more detail.

First, the average particle diameter of the particulates of the syndiotactic-1,2-polybutadiene resin used in the present invention needs to be in a range of 10 to 500 μm. The reason is that if the average particle diameter is l ss than 10 μm, tire performances n ice and roads as aimed at by the present invention are not suffici nt. On the oth r hand, if the average particle diameter is more than 500 μm, although some eff cts ar r cognized with resp ct to the tire p rformances n ice and snow, it is undesirabl because other performances such as wear resistance also required for the tire are deteriorated. The syndiotactic-1,2-polybutadiene resin used in

the present invention needs to be in th particulate form. The av rage ratio M between the major axis and the minor axis of the resin particulates is preferably not more than 6, more preferably not more than 4, in the state that the resin is kneaded into the rubber composition and when the maj r axis and the minor axis are measured as viewed in a circumferential section or a radial section of the tread. That is, in order to improve drivability or brakability on ice and snow, it is required that the syndi tactic-1,2-polybutadiene resin is dispersed in the rubber composition in the particulate form, not in the form of microorganic pile fibers.

The syndiotactic-1,2-polybutadiene resin has usually crystallinity. In the present invention, the crystalline syndiotactic-1,2-polybutadiene resin has a melting point of not less than 110°C. The reason is that if the melting point is less than 110°C, the resin is softened, deformed or partially or entirely melted when the resin is added and kneaded into the rubber component on compounding. Thus, since the desired average particle diameter cannot be maintained, improved tire performances on ice and snow as aimed at by the present invention disappear.

Further, it is necessary that 5 to 60 parts by weight of the above syndiotactic-1,2-polybutadiene resin is incorporated in the rubber composition for the tread of the pneumatic tire of the present invention relative to 100 parts by weight of the rubber component. The reason is that if the compounding ratio is less than 5 parts by weight, improved performances on ice and snow as desired can almost hardly be attained, whereas if more than 60 parts by weight of the resin is incorporated relative to 100 parts of the rubber component, other tire performances such as wear resistance are not only deteriorated, but also processability during the production of the tire is largely deteriorated, thereby rendering the pneumatic tire actually impractical.

In the present invention, it is unnecessary to limit the kind of the rubber component constituting the rubber composition in which the syndiotactic-1,2-polybutadiene resin is incorporated as well as the kinds of a filler and other chemical to any specific ones, and ordinary rubber, filler, chemical, etc. may be employed.

For example, as the rubber component, natural rubber, polyisoprene rubber, polybutadiene rubber, styrene-butadiene copolymer rubber, styrene-isoprenebutadiene terpolymer, styrene-isoprene copolymer rubber, and isoprene-butadiene copolymer rubber may be recited. The rubber composition used in the tread may include a filler, an antioxidant, a vulcanizing agent, a vulcanization accelerator, etc. The kinds and the amounts of these additives may be selected among the ordinary ranges, and are not limited to any specific ones.

According to the present invention, it is preferable that the tread rubber has closed cells at a foaming rate of 3 to 35 %. Such closed cells are effective in exhibiting excellent performances on ice and snow through increasing microscopic water absorption-drainage effect due to the cells in a state that ice is abundant with water melted on its surface near °C. The foaming may be effected either by using a foaming agent by or mixing with a gas under high pressure. If the foaming rate is less than 3%, the foaming effect cannot be sufficiently exhibited. On the other hand, if the foaming rate is more than 35%, the rigidity of the tread becomes insufficient. In this case, wear resistance lowers and occurrence of cracks on bottoms of grooves becomes greater.

The foaming rate Vs of the foamed rubber is expressed by the following formula: $Vs = \{(\rho o - \rho_1)/(\rho_1 - \rho_g) - 1\} \times 100(\%)$ ··· (1) in which ρ_1 is a density of the foamed rubber (g/cm^3), ρo is a density of a solid phase of the foamed rubber (g/cm^3), and ρ_g is a density of a gas phase inside the cells in the foamed rubber (g/cm^3). The foamed rubber is constituted by the solid phase, and voids (closed cells) defined by the solid phase, that is, a gas phase inside the cells. The density ρ_g of the gas phase is extremely small, i.e., almost near zero, and is extremely far smaller than the density ρ_1 of the solid phase. Therefore, the above formula (1) may be approximated to $Vs = \{(\rho o - \rho_1) - 1\} \times 100(\%)$.

In the pneumatic tire according to the present invention, the ordinary rubber or foamed rubber composition in which the above-mentioned syndiotactic-1,2-polybutadiene resin is incorporated may be arranged in a cap portion of the tread having a cap-and-base construction.

Next, the second aspect of the present invention will be explained in more detail.

As mentioned above, the syndiotactic-1,2-polybutadiene resin also employed in the second aspect of the present invention usually has crystallinity. The crystalline resin needs to have the melting point of not less than 110°C. The reason is that if the melting point is less than 110°C, the resin is softened, deformed or partially or entirely melted when the resin is added and kneaded into the rubber component on compounding. Thus, since the desired average particle diameter cannot be maintained, improved tire performances on ice and snow as aimed at by the present invention disappear.

Further, it is undesirable that (X + 10Y) is smaller than 250, because desired hardness of the resin-composite particulates cannot be obtained, so that intended performances on ice and snow cannot be obtained. On the other hand, it is undesirable that (X + 10Y) is greater than 1300, because processability is conspicuously deteriorated during the production of the resin-composite particulates.

Furthermor , th av rag partic diam ter of th particulates of the syndi tactic-1,2-polybutadiene resin used in th present invention n ed to b in a rang of 10 to 500 μm. The reason is that if th av rag particle diameter is less than 10 μm, tire performances n ice and roads as aimed at by the pres nt inv nti n are n t sufficient. On the other hand, if th av rage partic diameter is more than 500 μm, although some effects are

recognized with respect to th tire p rformances on ice and snow, it is undesirabl because other performances such as wear resistance also required for the tire are d teriorated.

Further, it is necessary that 5 to 60 parts by weight of the composite particulates of the above syndiotactic-1,2-polybutadiene resin is incorporated in the rubber composition for the tread of the pneumatic tire of the pres nt inv ntion relative to 100 parts by weight of the rubber compon nt. The reason is that if th compounding ratio is less than 5 parts by weight, improved performances on ice and snow as desired can almost hardly be attained, whereas if more than 60 parts by weight of the resin is incorporated relative to 100 parts of the rubber component, other tire performances such as wear resistance are not only deteriorated, but also processability during the production of the tire is largely deteriorated, thereby rendering the pneumatic tire actually impractical.

The composite particulates of the syndiotactic-1,2-polybutadiene resin satisfying the above-mentioned requirements to be used in the present invention can be produced by the following method by way of example.

Dewatered benzene, 760 cc, is charged into a 2-liter autoclave in which air is replaced by nitrogen gas, and 74 g of 1,3-butadiene is dissolved into benzene. To the solution is added 1 m mol cobalt octoate (a benzene solution containing 1 m mol/ml of cobalt octoate), and 1 minute thereafter 2 m mol triethyl aluminum (benzene solution containing 2 m mol/ml triethyl aluminum) is added and stirred. One minute later, acetone is added in an appropriate amount to attain a desired melting point. Further, one minute later, carbon dioxide, 0.6 m mol (benzene solution containing 0.3 m mol/ml) is added into the mixture, which is stirred at 10°C for 60 minutes to effect polymerization of 1,3-butadiene.

2,4-Ditertial-butyl-p-cresol, 0.75 g, is added to the syndiotactic-1,2-polybutadiene resin-produced liquid. Then, the resulting liquid is added into 1,000 ml of methanol, thereby precipitating a syndiotactic-1,2-polybutadiene resin.

The thus obtained syndiotactic-1,2-polybutadiene resin is further washed with methanol, and methanol is filtered off, followed by vacuum drying.

250 ml Given carbon black was added to the thus obtained resin, which is kneaded for three minutes at a temperature higher than a melting point of the resin by using a laboratory plastomill.

Composite particulates of the syndiotactic-1,2-polybutadiene resin having a given average particle diameter is obtained from the thus produced syndiotactic-1,2-polybutadiene resin-composite material by an ordinary method.

The method for producing the resin-composite particulates to be used in the present invention is not limited to the above-mentioned one, and any other appropriate producing method may be employed.

In the second aspect of the present invention, it is unnecessary to limit the kind of the rubber constituting the rubber composition in which the composite particulates of the syndiotactic-1,2-polybutadiene resin are incorporated as well as the kinds of a filler and other chemical to any specific ones, and ordinarily used rubber, filler, chemical, etc. may be employed.

For example, as the rubber component, natural rubber, polyisoprene rubber, polybutadiene rubber, styrene-butadiene copolymer rubber, styrene-isoprenebutadiene terpolymer rubber, styrene-isoprene copolymer rubber, and isoprene-butadiene copolymer rubber may be recited. The rubber composition used in the tread may include a filler, an antioxidant, a vulcanizator, a vulcanization accelerator, etc. The kinds and the amounts of these additives may be selected among the ordinary ranges, and are not limited to any specific ones.

According to the second aspect of the present invention, it is preferable that the tread rubber has closed cells at a foaming rate of 3 to 35 %. Such closed cells are effective in exhibiting excellent performances on ice and snow through increasing microscopic water absorption-drainage effect due to the cells in a state that ice is abundant with water melted on its surface near °C. The foaming may be effected either by using a foaming agent or by mixing with a gas under high pressure. If the foaming rate is less than 3%, the foaming effect cannot be sufficiently exhibited. On the other hand, the foaming rate is unfavorably more than 35%, because the rigidity of the tread becomes insufficient, so that wear resistance lowers and occurrence of cracks on bottoms of grooves becomes greater.

As mentioned above, the foamed rate of the foamed rubber is expressed by the following formula: $Vs = \{(\rho o - \rho_1)/(\rho_1 - \rho_g) - 1\} \times 100$ (%), which may be approximated to $Vs = \{(\rho o - \rho_1) - 1\} \times 100$(%). When the foamed rubber is employed as the matrix, the resin-composite particulates are dispersed in the foamed rubber.

In the pneumatic tire according to the second aspect of the present invention, the rubber composition including the above-mentioned syndiotactic-1,2-polybutadiene resin and composed of the non-foamed or foamed rubber as the matrix may be arranged in the entirety of the tread rubber or in only a cap portion of the tread having a cap-base construction.

In the following, the present invention will be explained with reference to examples and comparative examples.

First, methods for measuring various physical properti s of the exampl s and comparative examples will be explained.

1. Melting point of crystalline syndi tactic-1,2-polybutadien resin:

The resin was heated at a heating rate of 10°C/min in a temperature range from 30°C to 250°C, and an endothermic peak was obtained by using a differential thermal analyzer DSC 200 manufactured by SEIKO ELECTRONICS CO., LTD. The melting point of the resin was determined based on the thus btained endothermic peak.

2. Measurement of nitrogen-adsorption specific surface area of carbon black:

Nitrogen-adsorption specific surface area of carbon black was measured according to ASTM D3037-84.

3. Testing of physical properties of tread rubber:

(1) Measurement of coefficient of friction on ice

The coefficient of friction on ice of the rubber composition, particularly the coefficient of friction on ice near 0°C in a wet state, was measured with use of a dynamic-static friction coefficient meter manufactured by KYOWA KAIMEN KAGAKU, CO., LTD. by contacting a surface of a sample (sample dimensions: 10 mm long, 10 mm wide and 5 mm thick) obtained from a slab sheet produced by ordinary vulcanization with ice having a surface temperature of -0.5°C.

The measuring conditions were a load of 2 kgf/cm^2 and 5 kgf/cm^2 for a passenger car radial tire (small size tire) and a truck-bus radial tire (large size tire), respectively, a sliding speed of 10 mm/sec, a surrounding temperature of -2°C, and the ice surface state being substantially a mirror.

(2) Tests for performances of small size tires

Each small size tire PSR (165SR13) was prepared, subjected to ordinary running as idling over 50km, and tested to check each test item. Similar small tires were used in the following brakability test, wear resistance test and wet skid resistance test.

a) Brakability on ice:

Four tires to be tested were fitted to a vehicle having a displacement of 1500 cc, and a braked distance was measured on ice at an open temperature of -5°C.

In the following Experiment 1, test results are indicated by index, taking that of Comparative Example 1-1 as control tire as 100.

In the following Experiment 3, test results are indicated by index, taking that of Comparative Example 2-7 as control tire as 100.

The greater the value, the more excellent is the brakability on ice.

b) Wear resistance:

Two tires to be tested were fitted to a driving shaft of a passenger vehicle having a displacement of 1500 cc, and run on a concrete road in a test course at a given speed. Change in depth of a groove was measured. In Experiment 1, test results are indicated by index taking that of Comparative Example 1-1 as control tire as 100. In Experiment 3, test results are indicated by index, taking that of Comparative Example 2-7 as control tire as 100. The greater the value, the more excellent is the wear resistance.

c) Wet skid resistance:

Four tires to be tested were fitted to a vehicle having a displacement of 1500 cc, and rapidly braked from 80 km/h on a wet concrete road having water at a depth of 3 mm, and a distance required until the vehicle stopped after the tires were locked was measured. Skid resistance on wet road (wet skid resistance) of the tested tires was evaluated based on the following equation:

In Experiment 1,

$$\text{Wet skid resistance} = \frac{\text{Stopped distance of Comparative tire 1 - 1 as control tire}}{\text{Stopped distance of Test tire}} \times 100$$

In Experiment 3,

$$\text{Wed skid resistance} = \frac{\text{Stopped distance of Comparative Example 2 - 7 as control tire}}{\text{Stopped distance of test tires}} \times 100$$

The greater the value, the wet skid resistance is the more excell nt.

(3) Tests for performances of larg size tires:

Each large size tire TBR (1000R20) was prepared. Tires were fitted to a driving shaft of a 8-ton 2D type truck under a 100% loaded condition, subjected to ordinary running as idling over 150 km, and tested to check each test item.

a) Brakability on ice:

Four tires to be tested were fitted to all wheels of a 8-ton 2D-type truck under a 100% loaded condition, the tires were subjected to full lock braking from 20 km/h, and a braked distance at which the vehicle was stopped was measured. The temperature of ice was -5°C.

In the following Experiment 2, test results are indicated by index, taking that of Comparative Example 1-7 as control tire as 100.

In the following Experiment 4, a 6-ton 2D-type truck was used instead of the 8-ton 2D-type truck in Experiment 2. Test results are indicated by index, taking that of Comparative Example 2-8 as control tire as 100.

The greater the value, the more excellent is the brakability on ice.

b) Wear resistance:

Tires were fitted to entire wheels of the 8-ton 2D-type truck under a 100% loaded conditions, and actually run under ordinary conditions. Change in depth of a groove after 50,000 km running was measured. In Experiment 2, test results are indicated by index taking that of Comparative Example 1-7 as control tire as 100. In Experiment 4, test results are indicated by index, taking that of Comparative Example 2-8 as control tire as 100. The greater the value, the more excellent is the wear resistance.

In the following Table 1, the average particle diameters and the melting points of the crystalline syndiotactic-1,2-polybutadiene resins used in examples and comparative examples are shown.

The average particle diameter was measured by using an air jet sieve grain size meter, 200LS type manufactured by ALPINE Co., Ltd. 50% Accumulated particle diameter was taken as the average particle diameter.

Table 1

Kind of resin	A	B	C	D	E	F	G	H
Average particle diameter (μm)	2.5	18	80	120	310	570	120	120
Melting point of crystalline resin (°C)	140	121	194	139	170	137	87	106

Experiments 1 and 2

Each of Tables 2 and 3 shows a compounding recipe of various particulate syndiotactic-1,2-polybutadiene resins shown in Table 1 and rubber matrixes combined (parts by weight) as well as physical properties of vulcanizates of these particulate-containing rubbers and performances of tires in which each of the thus obtained particulate-mixed rubbers was employed in a tread of the tire. More particularly, Table 2 shows results of passenger radial tires (PSR) [Experiment 1], and Table 3 shows those of truck-bus radial tires (TBR)

[Experiment 2].

Table 2

		Comparative Example 1-1	Comparative Example 1-2	Example 1-1	Example 1-2	Example 1-3	Example 1-4	Comparative Example 1-3	Comparative Example 1-4	Comparative Example 1-5	Comparative Example 1-6	Example 1-5	Example 1-6
Compounding recipe	natural rubber	60	60	60	60	60	60	60	60	60	60	60	60
	butadiene rubber	40	40	40	40	40	40	40	40	40	40	40	40
	carbon black N220	60	60	60	60	60	60	60	60	60	60	60	60
	process oil	5	5	5	5	5	5	5	5	5	5	5	5
	stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	zinc oxide	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	antioxidant	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	vulcanization accelerator	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	sulfur	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
	foaming agent (ADCA)	-	-	-	-	-	-	-	-	-	3.0	3.0	3.0
	urea	-	-	-	-	-	-	-	-	-	2.8	2.8	2.8
	Kind of resin A		20	-	-	-	-	-	-	-	-	-	-
	B	-	-	20	-	-	-	-	-	-	-	-	-
	C	-	-	-	20	-	-	-	-	-	-	-	-
	D	-	-	-	-	20	-	-	-	-	-	10	20
	E	-	-	-	-	-	20	-	-	-	-	-	-
	F	-	-	-	-	-	-	20	-	-	-	-	-
	G	-	-	-	-	-	-	-	20	-	-	-	-
	H	-	-	-	-	-	-	-	-	20	-	-	-
Foaming rate (%)		-	-	-	-	-	-	-	-	-	17	14	16
Coefficient of friction on ice ×10-3		6.2	19	29	39	45	47	28	16	19	35	46	51
Tire performance	wet skid resistance	100	101	103	101	98	97	95	91	88	104	101	98
	brakability on ice	100	98	107	109	121	115	102	95	100	112	118	124
	wear resistance	100	109	106	95	102	99	79	91	89	88	97	95

Table 3

		Compar-ative Example 1-7	Compar-ative Example 1-8	Example 1-7	Example 1-8	Example 1-9	Example 01-1	Compar-ative Example 1-9	Compar-ative Example 1-10	Compar-ative Example 1-11	Example 1-11	C mpar-ativ Example 1-12
Compound-ing recipe	butadiene rubber	-	-	-	-	-	-	-	-	30	30	30
	natural rubber	100	100	100	100	100	100	100	100	70	70	70
	carbon black N110	45	45	45	45	45	45	45	45	55	55	55
	process oil	10	10	10	10	10	10	10	10	3	3	3
	stearic acid	2	2	2	2	2	2	2	2	4	4	4
	zinc oxide	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	3	3	3
	antioxidant	1	1	1	1	1	1	1	1	1	1	1
	vulcanization accelerator	1	1	1	1	1	1	1	1	2	2	2
	sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	foaming agent (OBSH) Note 1	-	-	-	-	-	-	-	-	4.0	4.0	4.0
	amount of resin D	-	3	10	20	30	50	70	100	3	30	70
Foaming rate (%)		-	-	-	-	-	-	-	-	14	16	19
Coefficient of friction on ice $\times 10^{-2}$		23	22	32	48	53	45	37	30	43	50	39
Tire perform-ance	brakability on ice	100	97	108	113	119	115	104	*	112	122	*
	wear resistance	100	106	101	102	98	97	86	*	93	92	*

Note 1 : p,p'-oxybis(benzylsulfonylhydrazide)

Tabl 2 shows test results in th performance-evaluating tests for the passenger car radial tires, and the following is confirmed from this Table 2.

That is, in Examples 1-1 to 1-4, the syndiotactic-1,2-polybutadiene resin B, C, D or E satisfying the requirements of the present inventi n with respect to the average partid diameter and the melting point of the crystalline resin was incorporated in an amount of 20 parts by weight. In Comparative Examples 1-2 to 1-5, the resin A, F, G or H not satisfying such requirements was incorporated. As compared with Comparative Examples 1-2 to 1-5, it is seen from Table 2 that Examples 1-1 to 1-4 had largely improved brakability on ice, while almost not deteriorating wet skid resistance or wear resistance. (The results are compared through Comparative Example 1-1 as control tire).

In Examples 1-5 and 1-6, the syndiotactic-1,2-polybutadiene resin D satisfying the above requirements of the present invention was compounded into the tread rubber, and a foamed rubber was used as the matrix rubber. In Examples 1-5 and 1-6, the brakability on ice could be further improved without almost deteriorating other tire performances. In Comparative Example 1-6, no such a resin was compounded, but a foamed rubber was used alone. In Comparative Example 1-6, the brakability on ice was improved, but wear resistance was not satisfactory.

Next, Table 3 shows test results in the performance-evaluating tests for the truck-bus radial tires, and the following is confirmed from this Table 3.

In Examples 1-7 to 1-10, the syndiotactic-1,2-polybutadiene resin D satisfying the requirements of the present invention was incorporated into a tread rubber in a compounding recipe specified in the present invention. In Comparative Examples 1-8 to 1-10, the compounding ratio of the resin D fell outside the range in the present invention. As compared with Comparative Examples 1-8 to 1-10, the brakability on ice was largely improved in Examples 1-7 to 1-10, while wear resistance is not almost lost. (The results are compared through Comparative Example 1-7 as control tire).

In Example 1-11, the syndiotactic-1,2-polybutadine resin D satisfying the requirements of the present invention was incorporated into a tread rubber in a compounding recipe specified in the invention, and a foamed rubber was used as the matrix rubber. In Example 1-11, brakability on ice could be further improved, while not almost deteriorating other tire performances. In Comparative Examples 1-11 and 1-12, the resin was incorporated in an amount falling outside the compounding recipe specified in the present invention, although a foamed rubber was used. In Comparative Examples 1-11 and 1-12, brakability on ice was improved, but satisfactory wear resistance could not be obtained.

As mentioned above, according to the first aspect of the present invention, since the rubber composition in which the particulates having the specific structure are incorporated in a given amount is used as the rubber composition for the tread, satisfactory drivability and brakability are remarkably improved in dry-on-ice conditions as well as in wet-on-ice conditions, while cornering stability, durability and low fuel consumption required in the summer season or during running on ordinary roads are not almost deteriorated. Therefore, the pneumatic tire according to the present invention can be called the all-season tire in a real sense.

In the following, the second aspect of the present invention, will be explained with reference to specific examples.

Experiment 3

The compounding recipe and test results of tread rubbers will be shown in Tables 4 (Examples 2-1 through 2-10) and Table 5 (Comparative Examples 2-1 through 2-8). This Experiment 3 relates to the tests for performances of the above-mentioned small size tires.

In Examples 2-1 through 2-8 of Experiment 3, the matrix other than the particulates was a non-foamed rubber, and a foamed rubber was used in Examples 2-9 and 2-10.

Kinds and physical properties of the resin-composite particulates in Tables 4 and 5 are shown in Table 6. The resin-composite particulates A through H fall in the scope of the present invention, and the resin-composite particulates I through M fall outside the scope of the invention.

Table 4

			Example									
			2-1	2-2	2-3	2-4	2-5	2-6	2-7	2-8	2-9	2-10
Compounding recipe	natural rubber		60	60	60	60	60	60	60	60	60	60
	butadiene rubber		40	40	40	40	40	40	40	40	40	40
	carbon black N220		60	60	60	60	60	60	60	60	60	60
	process oil		5	5	5	5	5	5	5	5	5	5
	stearic acid		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	zinc oxide		3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	antioxidant		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	vulcanization accelerator		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	sulfur		1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
	foaming agent (ADCA)		-	-	-	-	-	-	-	-	3.0	3.0
	urea		-	-	-	-	-	-	-	-	2.8	2.8
	resin-composite particulates	kind	A	B	C	D	E	F	G	H	B	B
		amount	20	20	20	20	20	20	20	20	20	10
physical property of tread rubber	foaming rate (%)		-	-	-	-	-	-	-	-	19	18
	coefficient of friction on ice $\times 10^{-2}$		5.3	5.7	5.8	6.0	5.1	5.9	6.1	5.0	6.4	6.1
Tire performance	wet skid resistance		103	102	100	100	103	101	101	100	104	103
	brakability on ice		129	134	135	136	127	135	138	127	143	139
	wear resistance		101	100	99	99	101	100	99	100	97	99

Table 5

			Comparative Example						
			1-1	1-2	1-3	1-4	1-5	1-6	1-7
Compounding recipe	natural rubber		60	60	60	60	60	60	60
	butadiene rubber		40	40	40	40	40	40	40
	carbon black N220		60	60	60	60	60	60	60
	process oil		5	5	5	5	5	5	5
	stearic acid		1.5	1.5	1.5	1.5	1.5	1.5	1.5
	zinc oxide		3.0	3.0	3.0	3.0	3.0	3.0	3.0
	antioxidant		1.0	1.0	1.0	1.0	1.0	1.0	1.0
	vulcanization accelerator		1.5	1.5	1.5	1.5	1.5	1.5	1.5
	sulfur		1.8	1.8	1.8	1.8	1.8	1.8	1.8
	foaming agent (ADCA)		-	-	-	-	-	-	-
	urea		-	-	-	-	-	-	-
	resin-composite particulates	kind	I	J	K	L	M	B	-
		amount	20	20	20	20	20	3	-
physical property of tread rubber	foaming rate (%)		-	-	-	-	-	-	-
	coefficient of friction on ice $\times 10^{-2}$		4.4	4.5	4.3	3.2	4.5	2.1	2.1
Tire performance	wet skid performance		99	98	98	99	98	101	100
	brakability on ice		121	120	119	108	121	100	100
	wear resistance		101	99	100	100	102	101	100

Table 6

Kind of resin-composite particulates		A	B	C	D	E	F	G	H	I	J	K	L	M
Average particle diameter of resin-composite particulates (μm)		120	120	120	120	120	120	310	18	120	120	2.5	120	120
Melting point of crystalline resin (°C)		140	140	140	140	140	140	170	140	140	140	140	87	140
Master batch of carbon black	N_2 specific surface area X m^2/g	83	114	143	197	114	114	114	114	42	114	114	114	82
	Y weight parts (PHR)	50	50	50	50	20	70	50	50	20	10	50	50	16
	X + 10Y	583	614	643	697	314	814	614	614	242	214	614	614	242

As mentioned abov , in Examples 2-1 through 2-10, the coeffici nt of friction on ice of th tread rubber could be made far greater as compared with the comparative xamples, while wear resistance or wet skid resistance was n t deteriorated. Thus, it is s en that wh n such a rubber composition is used in the pneumatic

tire, brakability on ice can be largely improv d.

Particularly, it is seen that in Examples 2-9 and 2-10 using the foamed rubber as the matrix of the tread rubber, brakability n ice and w t roads could be remarkably improved.

To th contrary, in Comparative Examples 2-1 through 2-6, the resin-composite particles I to M were incorporated, and in Comparativ Example 3-7, the compounding ratio of th particulates fell outside th scope of the present invention. In these Comparative Examples 2-1 through 2-6 and 3-7, brakability on ice and wet roads was at low levels.

Experiment 4:

Table 7 shows the compounding recipe and test results of tread rubbers (Examples 2-11 through 2-13 and Comparative Examples 2-8 through 2-11). Experiment 4 relates to test results of performances of the above-mentioned large size tires.

In Examples 2-11 and 2-12 of Experiment 4, the matrix other than the particulates was a non-foamed rubber, and in Example 2-13, the matrix was a foamed rubber.

The kinds of the resin-composite particulates are shown in Table 6.

Table 7

		Example 2-11	Example 2-12	Example 2-13	Comparative Example 2-8	Comparative Example 2-9	Comparative Example 2-10	Comparative Example 2-11
Compounding recipe	natural rubber	100	100	100	100	100	100	100
	carbon black N110	45	45	45	45	45	45	45
	process oil	10	10	10	10	10	10	10
	stearic acid	2	2	2	2	2	2	2
	zinc oxide	2.5	2.5	2.5	2.5	2.5	2.5	2.5
	antioxidant	1	1	1	1	1	1	1
	vulcanization accelerator	1	1	1	1	1	1	1
	sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	foaming agent (OBSH)	-	-	4.0 (foaming rate 19%)	-	-	-	-
	resin-composite particulates: kind	B	F	B	-	J	I	M
	resin-composite particulates: amount	20	20	15	-	20	20	20
Physical property of tread rubber	coefficient of friction on ice x10-2	6.0	5.9	6.3	2.3	5.3	4.8	4.8
Tire performance	brakability on ice	127	130	137	100	115	113	111
	wear resistance	101	99	96	100	97	96	99

As shown above, in Examples 2-11 through 2-13, the coefficient of friction on ice of the tread rubber was far increased as compared with Comparative Examples, while wear resistance was not deteriorated. Thus, when th rubb r composition in any ne of Exampl s 2-11 through 2-13, brakability on-ice can by remarkably improved.

In particular, it is seen that in Exampl 2-13 using the foamed rubb r in the matrix of the tread rubber, brakability on ice has been greatly improved.

To the contrary, Comparative Example 2-8 containing n resin particulates and Comparative Examples 2-9 and 2-11 containing the particulates falling outside the scope of the present invention, brakability on ic was at low levels.

As mentioned abov , since the pn umatic tire of the present invention uses, as the tread rubber, the rubber compositi n in which a given amount f resin-composite particulates composed f th syndiotactic-1,2-polybutadiene resin and the carbon black are used and optionally further the matrix of the rubber composition other than the particulates is made of the formed rubber, the present invention can actually provide the so-called all season tire and the studless tires having drivability and brakability on dry-on-ice road as well as on wet-on-ice roads remarkably improved, while neither cornering stability nor wear resistance in the summer season are deteriorated.

Claims

1. A pneumatic tire having a tread composed of a rubber composition, said rubber composition including a rubber component and particulates of a crystalline syndiotactic-1,2-polybutadiene resin or particulates of specific syndiotactic-1,2-polybutadiene resin-composite material, the particulates having an average particle diameter of 10 to 500 μm, the melting point of said crystalline syndiotactic-1,2-polybutadiene resin being not less than 110°C, and the compounding ratio of the said resin being 5 to 60 parts by weight relative to 100 parts by weight of said rubber composition.

2. A pneumatic tire as claimed in claim 1,
characterized in that a matrix portion of the rubber composition of the tread rubber is a foamed rubber.

3. A pneumatic tire as claimed in claim 1,
characterized in that the particulates having an average particle diameter of 10 to 500 μm are resin-composite particulates composed of a crystalline syndiotactic-1,2-polybutadiene resin having a melting point of not less than 110°C and a carbon black, the compounding ratio of the resin-composite particulates being 5 to 60 parts by weight relative to 100 parts by weight of the rubber component, and the resin and the carbon black satisfying the following inequalities: $250 < X + 10Y < 1300$ in which X is nitrogen-adsorption specific surface area (unit: m^2/g) and Y is compounding ratio of the carbon black (parts by weight) relative to 100 parts by weight of the resin.

4. A pneumatic tire as claimed in claim 3,
characterized in that the rubber component constituting a matrix portion of the rubber composition of the tread rubber other than the particulates is a foamed rubber.

5. A pneumatic tire as claimed in any of claims 1 to 4,
characterized in that the tread has a cap-and-base construction, and said rubber composition is used in the cap.

6. A pneumatic tire as claimed in any of claims 1 to 5,
characterized in that a foaming rate of the tread rubber is 3 to 35.

7. A pneumatic tire as claimed in any of claims 1 to 6,
characterized in that an average ratio between a major axis and a minor axis of the resin particulates is not more than 6.

8. A pneumatic tire as claimed in any of claims 1 to 7,
characterized in that the rubber component is selected from natural rubber, polyisoprene rubber, polybutadiene rubber, styrene-butadiene copolymer rubber, styrene-isoprene-butadiene terpolymer, styrene-isoprene copolymer rubber, and isoprene-butadiene copolymer rubber.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 5174

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	WORLD PATENTS INDEX LATEST Week 8819, Derwent Publications Ltd., London, GB; AN 88-130660 & JP-A-63 075 046 (TOYO RUBBER) 5 April 1988 * abstract *	1,8	B60C1/00 C08L21/00 //(C08L21/00, 9:00)
A	DE-A-3 703 480 (BRIDGESTONE CORP.) * abstract; table 9 * * page 4, line 60 - line 63 *	1-8	
A	US-A-4 274 462 (OGAWA ET AL.) * abstract; claims * * column 2, line 20 - line 36 * * tables 1,2 *	1,3,5,7,8	
A	EP-A-0 307 341 (GOODYEAR TIRE & RUBBER CO.) * abstract * * page 3, line 4 - line 13 * * page 3, line 49 - line 55 *	1,8	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

B60C
C08L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	08 SEPTEMBER 1992	METTLER R.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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